THE JOURNAL
OF
CHEMICAL PHYSICS

VOLUME 13, NUMBER 4 APRIL, 1945

The Thermal Expansion and Compressibility of a Three-Dimensional System of Harmonic Oscillators

F. A. MATSEN AND JOHN E. WALKEY
Departments of Chemistry and Chemical Engineering, The University of Texas, Austin, Texas

(Received October 13, 1944)

Thermal expansions and compressibilities are calculated from equations of state of the Grüneisen form which are derived from a general partition function. The non-thermal energy and frequency are obtained as functions of volume, the constants in these functions being evaluated from data on the second virial coefficients of gases. Data of state are calculated for three types of thermal energy distributions, the classical, the Einstein, and the Debye. A limitation on the harmonic oscillator approximation is discussed as is the quantal effect in the law of corresponding states.

THE harmonic oscillator model has long been used as a first approximation in theories of liquids and solids.[1] In this model monatomic molecules are assumed to vibrate independently with a Hooke's law restoring force. The potential energy, U, consists of two terms, the potential energy of the molecules in their equilibrium positions, U_0, and the potential energy due to the displacement, r, of the molecules from these positions.

$$U=U_0+2\pi^2m\nu^2r^2, \tag{1}$$

where ν and m are the average frequency of oscillation and the mass, respectively, U_0 and ν being functions of the volume.

[1] Among the more recent papers dealing with properties of state based on the harmonic oscillator model are: (a) K. F. Herzfeld and M. Goeppert-Mayer, Phys. Rev. **46**, 995 (1934); (b) L. Brillouin, Trans. Faraday Soc. **33**, 54 (1937); (c) J. F. Kincaid and H. Eyring, J. Phys. Chem. 37 (1938); (d) M. Born, J. Chem. Phys. **7**, 591 (1939); (e) G. Kane, J. Chem. Phys. **7**, 603 (1939); (f) O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941); (g) J. Walter and H. Eyring, J. Chem. Phys. **9**, 393 (1941); (h) F. A. Matsen and G. M. Watson, J. Chem. Phys. **11**, 343 (1943); (i) O. K. Rice, J. Chem. Phys. **12**, 289 (1944); (j) M. M. Gow, Proc. Camb. Soc. **40**, 151 (1944); (k) R. Fürth, Proc. Roy. Soc. **183A**, 87 (1944).

If the system is considered quantal the zero point energy, $3h\nu/2$ must be included. Thus, U' may be substituted for U defined above.

$$U'=U_0+3h\nu/2+2\pi^2m\nu^2r^2. \tag{2}$$

In this simple system the volume is a minimum at absolute zero, at which temperature the molecules are motionless if the system is classical, or possess the lowest amplitude of vibration if the system is quantal. As the temperature is increased the amplitude of the vibrations increases with the result that the volume increases.

The Grüneisen equation of state may be obtained from the following general partition function for the solid state,

$$Q=K(\theta/T)\exp\{-U_0/kT\}. \tag{3}$$

Here θ is the Debye temperature $h\nu/k$, and U_0 has the same significance as in Eq. (1).

$$P=kT(\delta\ln Q/\delta V)_T=-(\delta U_0/\delta V)_T +kT(\delta\ln K(\theta/T)/\delta V)_T. \tag{4}$$

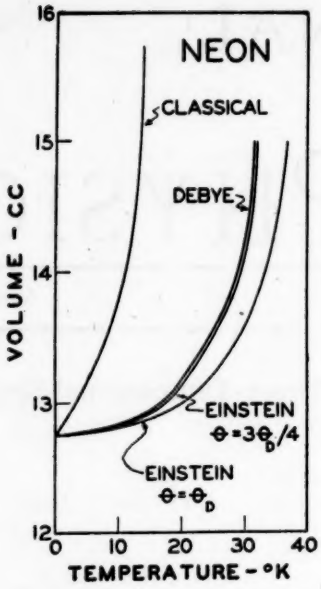

FIG. 1. Thermal expansion of neon, zero point energy neglected.

Now

$$kT(\delta \ln K(\theta/T)/\delta V)_T = -kT^2(\delta \ln K(\theta/T)/\delta T)_V(\delta \ln \theta/\delta V)_T = -E(T)(\delta \ln \theta/\delta V)_T.^2 \quad (5)$$

On substitution of Eq. (5) the equation of state becomes

$$P = -(\delta U_0/\delta V)_T - E(T)(\delta \ln \theta/\delta V)_T; = -(\delta U_0/\delta V)_T - E(T)(\delta \ln \nu/V)_T,$$

since

$$\theta = h\nu/k. \quad (6)$$

At zero pressure

$$E(T) = -[(\partial U_0/\partial V)_T]/[(\partial \ln \nu/V)_T]. \quad (7)$$

---

[2] $$d \ln K(\theta/T) = \frac{d \ln K(\theta/T)}{d(\theta/T)} d(\theta/T).$$

Then

$$\left(\frac{\delta \ln K(\theta/T)}{\delta T}\right)_V = \frac{d \ln K(\theta/T)}{d(\theta/T)}\left(\frac{\delta(\theta/T)}{\delta T}\right)_V = \frac{-d \ln K(\theta/T)}{d(\theta/T)} \frac{\theta}{T^2},$$

and

$$\left(\frac{\delta \ln K(\theta/T)}{\delta V}\right)_T = \frac{d \ln K(\theta/T)}{d(\theta/T)}\left(\frac{\delta(\theta/T)}{\delta V}\right)_T = \frac{d \ln K(\theta/T)}{d(\theta/T)} \frac{\theta}{T}\left(\frac{\delta \ln \theta}{\delta V}\right)_T.$$

Then

$$kT\left(\frac{\delta \ln K(\theta/T)}{\delta V}\right)_T = -kT^2\left(\frac{\delta \ln K(\theta/T)}{\delta T}\right)_V\left(\frac{\delta \ln \theta}{\delta V}\right)_T = -E(T)\left(\frac{\delta \ln \theta}{\delta V}\right)_T.$$

Inclusion of the zero point energy may be made by writing the partition function

$$Q = K(\theta/T) \times \exp[(-U_0 + \tfrac{3}{2}h\nu)/kT], \quad (8)$$

which leads to

$$P = -(\delta U_0/\delta V)_T - E(T)(\partial \ln \nu/\partial V)_T - \tfrac{3}{2}h(\partial \nu/\partial V)_T. \quad (9)$$

At zero pressure

$$E(T) = -\frac{(\partial U_0/\partial V)_T + \tfrac{3}{2}h(\partial \nu/\partial V)_T}{(\partial \ln \nu/\partial V)_T} = \frac{-(\partial U_0/\partial V)_T}{(\partial \ln \nu/\partial V)_T} - \tfrac{3}{2}h\nu. \quad (10)$$

This equation has been derived by several other methods.[1a,1f,3]

Three forms of the thermal energy, $E(T)$, will be used:[4]

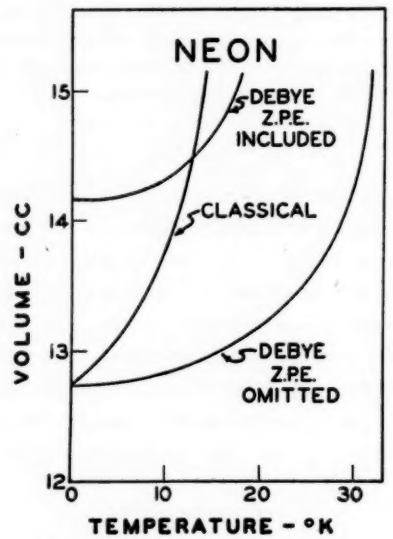

FIG. 2. Thermal expansion of neon, with and without zero point energy.

---

[3] E. Grüneisen, *Zustand des festen Korpers, Handbuch der Physik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1926), Vol. X. See also Vol. XXIV/2.

[4] Derived from the following partition functions:

a. Classical: $K(\theta/T) = (T/\theta)^3$;

b. Einstein: $K(\theta/T) = (1-e^{-\theta/T})^{-3}$;

c. Debye: $\ln K(\theta/T) = \ln(1-\exp[-\theta_D/T])^{-3} + 3\frac{T^3}{\theta_D^3}\int_0^{\theta_D/T} \frac{X^3}{e^x-1}dX.$

$\theta_D = h\nu_m/k$ where ν_m is the maximum frequency in the Debye frequency spectrum. It is related to the average frequency, ν, by the approximate relation $\nu = \frac{3}{4}\nu_m$.

a. Classical

$$E(T)=3kT; \tag{11}$$

b. Einstein

$$E(T)=3kT\left(\frac{\theta/T}{e^{\theta/T}-1}\right); \tag{12}$$

c. Debye

$$E(T)=9kT(T/\theta_D)^3\int_0^{\theta_D/T}\frac{X^3}{e^X-1}dX. \tag{13}$$

Both U_0 and ν are functions of the volume; however, it is more convenient to use the distance between the equilibrium positions of the molecules, a, related to the volume by the following equation:

$$V=Na^3/\gamma,$$

where γ is the packing factor equal to $\sqrt{2}$ for face-centered structures.

CALCULATION

In an earlier paper[1h] U_0 and ν were obtained as functions of a by averaging a Morse function for the potential energy of a pair of molecules, one molecule moving over the surface of a sphere of radius r, the center of the sphere being at the equilibrium position of that molecule while the other molecule is fixed a distance a away. When this average was multiplied by one-half the number of nearest neighbors, the quantity U was obtained.

$$U=\frac{CA}{2n^2a}\Big\{\frac{\exp\left[-2n(a-R_1)\right]}{4}\times\left[\left(\frac{2na+1}{r}\right)\sinh 2nr-2n\cosh 2nr\right]-2\exp\left[-n(a-R_1)\right]\times\left[\left(\frac{na+1}{r}\right)\sinh nr-n\cosh nr\right]\Big\}. \tag{14}$$

On expansion in terms of r this yields

$$U=\frac{CA}{2}\{\exp\left[-2n(a-R_1)\right]-2\exp\left[-n(a-R_1)\right]\}+\frac{CA}{6a}2\exp\left[-2n(a-R_1)\right](n^2a-n)-\exp\left[-n(a-R_1)\right](n^2a-2n)\}r^2, \tag{15}$$

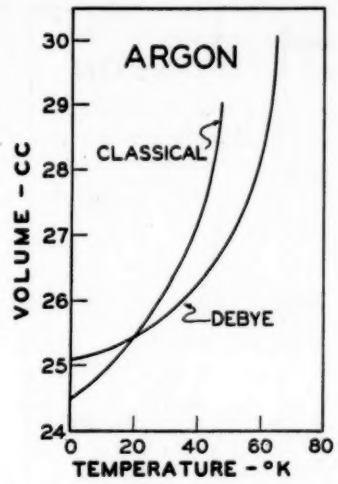

FIG. 3. Thermal expansion of argon.

the terms containing r^4 and higher being neglected. The use of the expanded form and the neglect of the higher order terms causes Eq. (15) to be a less exact description of the potential energy for large values of a. This effect will be discussed later in connection with the calculations on the thermal expansion and compressibility. Values of the constants A, n, and R_1 were obtained from second virial coefficient data via Lennard-Jones and Devonshire[5] and Buckingham.[5]

On comparison with Eq. (1) it may be seen that

$$U_0=\frac{CA}{2}\{\exp\left[2n(a-R_1)\right]-2\exp\left[n(a-R_1)\right]\}, \tag{16}$$

and

$$2\pi^2m\nu^2=\frac{CA}{2a}\cdot\tfrac{1}{3}\{2\exp\left[-2n(a-R_1)\right](n^2a-n)-\exp\left[-n(a-R_1)\right](n^2a-2n)\}. \tag{17}$$

Equation (17) may be expressed in terms of U_0.

$$2\pi m\nu^2=\frac{1}{3}\left\{\frac{1}{2}\frac{d^2U_0}{da_2}+\frac{1}{a}\frac{dU_0}{da}\right\}, \tag{18}$$

as the simple differentiation of U_0 will show.

[5] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A163**, 53 (1937); R. A. Buckingham, ibid. **A168**, 264 (1938). Both of these references are quoted by R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Macmillan Company, New York, 1939).

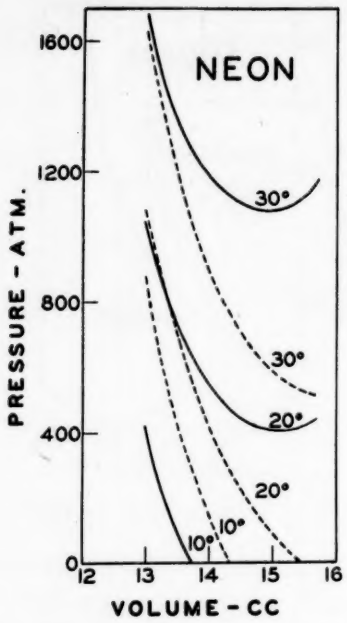

FIG. 4. Dotted lines, classical behavior; full lines, quantal behavior.

Originally the authors did not consider this to be a general equation but peculiar to the Morse form of U_0. However, it was later pointed out[6] that Eq. (18) can be derived for any analytic U_0: See appendix. Since differentiation is simpler with the Lennard-Jones form than with the Morse, the former will be used.

$$U_0=\frac{C}{2}\left(\frac{u}{a^{12}}-\frac{v}{a^6}\right), \tag{19}$$

where u and v are constants evaluated in reference (5). Then

$$\frac{dU_0}{da}=\frac{3C}{a^{13}}(va^6-2u), \tag{20}$$

$$\nu^2=(-C/4\pi^2m)(5va^6-22u), \tag{21}$$

and

$$\frac{d\ln\nu}{da}=\frac{1}{2}\frac{d\ln\nu^2}{da}=-\frac{1}{2a}\frac{(40va^6-308u)}{(5va^6-22u)}. \tag{22}$$

Finally from Eq. (7)

$$E(T)=\frac{6C}{a^{12}}\frac{(va^6-2u)(5va^6-22u)}{(40va^6-308u)}, \tag{23}$$

and from Eq. (9)

$$E(T)=\frac{6C}{a^{12}}\frac{(va^6-2u)(5va^6-22u)}{(40va^6-308u)}-\frac{3h}{2}\left[\frac{-C}{4\pi^2M}(5va^6-22u)\right]^{\frac{1}{2}}. \tag{24}$$

The temperature corresponding to a given value of a may now be calculated for the various energy distributions. For the classical distribution the right side of Eq. (23) divided by $3k$ gives the temperature directly. For the Einstein and Debye distributions the right side of Eqs. (22) and (24) divided by T and values of $(E-E_0)/T$ obtained from the *Landolt-Bornstein Tabellen* for each distribution are plotted against θ/T.[7] The Debye temperatures, θ_D were obtained from the same tables, that for argon being 85° and for neon 63°. The temperature was calculated from the value of θ/T at the intersection of the two curves. The results are plotted in Figs. 1 to 3.

In Fig. 1 the thermal expansions resulting

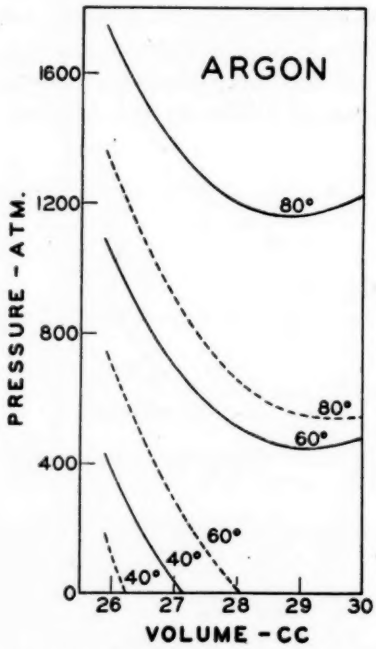

FIG. 5. Dotted lines, classical behavior; full lines, quantal behavior.

[6] Private communication from K. F. Herzfeld.

[7] θ_D is here regarded as an experimental constant chosen so as to fit experimental C_V data. Variation of θ_D is small compared to the variation of temperature so that θ/T may be regarded as a function of T only. See Fowler and Guggenheim, reference 5, pp. 146–149.

from the three energy distributions are compared. In Figs. (2) and (3) the zero point energy is included as formulated in Eq. (24).

Equations (6) and (9), taking a and T as independent variables, yield Figs. 4 and 5.

LIMITATIONS OF THE HARMONIC OSCILLATOR MODEL

Rice,[1i] employing specific heat data to calculate a total energy from which he subtracts the thermal energy and zero point energy, has obtained the potential energy of a pair of argon molecules. This potential energy when plotted against the distance between molecules has a very different appearance from the one which is obtained from second virial coefficient data. See Fig. 6. He states that this discrepancy may be caused by the deviation of the solid from true harmonic oscillator behavior, which is to be expected only for small vibrations. He states further that even at absolute zero, the zero point vibrations may be large enough to cause serious deviation. In consequence it would seem that the foundation of the Debye theory and the Grüneisen equation which are based on the harmonic oscillator model is less secure than is generally recognized.

The results of this research are in accord with Rice's view of the limited applicability of the harmonic oscillator model. Equation (14) for the potential energy of an oscillator takes the harmonic oscillator form only after expansion and cutting off the expansion at r^2. Consequently this formulation of the potential energy indicates that these systems can be harmonic oscillators only at small volumes and that the equations of state derived do not apply at larger volumes. This effect appears as an almost vertical thermal expansion curve and a minimum in the compressibility curve at larger volumes. When zero point energy is included the effect is more pronounced as may be seen in Fig. 2 for neon, only a small portion of the curve being significant. For hydrogen and helium the effect is even more pronounced, the zero point vibration being so great that the resultant large volume invalidates the harmonic oscillator formulation even at absolute zero.

It is interesting to note that infinite thermal expansion at larger volumes from the harmonic oscillator model have been obtained by Herzfeld and Goeppert-Mayer,[1a] Born,[1d] Kane,[1e] Gow,[1j] and Fürth,[1k] employing more elaborate developments. The first of these authors have considered

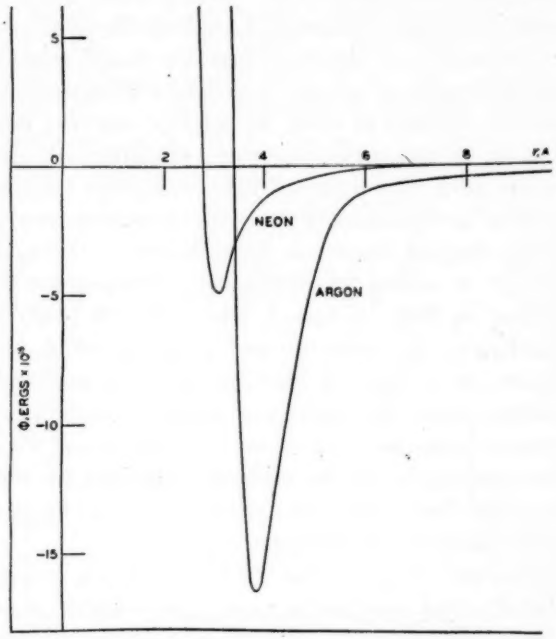

FIG. 6. Potential energy of a pair of molecules as a function of their intermolecular distance.

the solid to be unstable at the point of infinite thermal expansion and have associated this point with the melting point of the solid, obtaining rather good agreement. If this were a legitimate association the harmonic oscillator could be regarded a good model up to the melting point. Fürth has examined this association in detail and has come to the conclusion that it is not justified, pointing out that solids would have high thermal expansions near the melting point on the basis of theory, when experimentally they do not.[8] The harmonic oscillator model, therefore, does not describe the behavior of solids at larger volumes.

[8] Fürth points out as further argument against the association that the ratio of calculated volume change from absolute zero to instability point to the experimental volume change from absolute zero to the melting point is always greater than one. The authors believe, however, that this is not a valid argument in the case of the inert gases since Fürth, treating the problem classically, does not take into account the effect of zero point energy on the volume. See Fig. 2.

DISCUSSION OF RESULTS

In Fig. (1) the thermal expansions resulting from the three energy distributions are compared. The Einstein form with $\theta = 3\theta_D/4$ is practically identical with the Debye form and need not be discussed separately. The classical form gives a higher thermal expansion than does the quantal.

Classically at absolute zero one would expect the molecules to occupy positions corresponding to the minima in their interaction curves. See Fig. 6. If the molecules were vibrating at absolute zero by virtue of their zero point energy it is to be anticipated that the molecules would move farther apart as they do when thermal energy is added to the system. This effect is shown in Figs. 2 and 3. The effect is greater the lighter the molecule and as was pointed out above, is so large in the case of hydrogen and helium that the harmonic oscillator equation cannot be applied. This may explain in part why the experimental molar volumes of helium, hydrogen, and neon are larger than one would expect from their interaction curves.

In Figs. 4 and 5 the PVT curves are given, the classical solid being more compressible than the Debye solid. The deviation of quantal from classical behavior with regard to compressibility and thermal expansion is less for argon than for neon.

APPLICATION TO THE LAW OF CORRESPONDING STATES

Neon, hydrogen and helium are abnormal liquids in that their properties deviate markedly from those predicted by the law of corresponding states, the deviation being commonly ascribed to quantal effects. Pitzer[9] has formulated the conditions which must be fulfilled to apply the law of corresponding states. The conditions relative to this discussion are that classical statistical mechanics must apply and that the potential energy between pairs of molecules must be a universal function of R/R_1 where R is the distance between the molecules and R_1 is the position of minimum in the potential function. See Fig. 6. The statement is then made that properties of liquids should be compared at temperatures such that the ratios of the volume of the gas to the volume of the liquid are equal. When this is carried out neon, hydrogen and helium deviate markedly from normal behavior.[10]

For a given reduced temperature the ratio $V_{\text{gas}}/V_{\text{liquid}}$ should be a constant for all normal liquids. However, for neon, hydrogen, and helium this volume ratio is lower than for normal liquids, indicating that the volume of the liquid is abnormally high. This is borne out qualitatively by the fact that in this research the quantal volume was found to be larger than the classical (i.e., normal behavior) at low temperatures. The effect was found to be smaller for argon than for neon. The difference between the classical and the quantal volumes becomes smaller at higher temperatures due to the greater thermal expansion of the classical system, the quantal behavior becoming identical with the classical behavior at higher temperatures. Since argon is a liquid at higher temperatures and heavier than neon, these two effects combine to make argon a more normal liquid. By similar argument helium and hydrogen are less normal.

The fact that quantal volumes are larger than classical volumes affects the comparison of other properties, though not markedly. Pitzer[9] has pointed out that this can account for only about 1/7 of the total discrepancy (0.7 cal./mole/degree) in the entropy of vaporization of neon, the remaining difference coming from the quantal effect on the entropy itself.[11]

APPENDIX

Let $\phi(a)$ be the potential energy of a pair of molecules, a distance $a^2 = \sum_i^3 x_i^2$ apart. The Taylor expansion in three coordinates about $a = a^1$, and neglecting cross differentials is

$$\phi = \phi(a^1) + \sum_i^3 \left(\frac{\partial \phi}{\partial x_i}\right)_{a^1} dx_i + \frac{1}{2}\sum_i^3 \left(\frac{\partial^2 \phi}{\partial x_i^2}\right)_{a^1} dx_i^2 + \cdots.$$

From this expansion may be calculated the average potential energy $\bar{\phi}$ of the pair of molecules for a displacement da from the reference distance a^1.

[9] K. S. Pitzer, J. Chem. Phys. **7**, 583 (1939).

[10] Quantal effects are important for light molecules and low comparison temperature, these two factors seeming to go together in that light molecules also have shallow interaction curves and consequently are liquids at low temperatures only.

[11] A very approximate calculation of the difference between entropy of a quantal and that of a classical system may be made. At 20°K for neon, with $\theta_D = 63$ and $\theta = 48$,

$$S_{\text{Debye}}(\theta_D) - S_{\text{Classical}} = S_{\text{Debye}}(\theta_D) - 3R - 3R \ln (T/\theta) = 1.5 \text{ cal./mole/degree}$$

Now

$$\partial\phi/\partial x_i=(\partial\phi/\partial a)(x_i/a)$$

and

$$\frac{\partial^2\phi}{\partial x_i^2}=\frac{d^2\phi}{da^2}\frac{x_i^2}{a^2}+\frac{1}{a}\left(1-\frac{x_i^2}{a^2}\right)\frac{d\phi}{da}.$$

Replacing x_i/a and x_i^2/a^2 by their average values 0, and $\frac{1}{3}$ respectively,

$$\overline{\frac{\partial\phi}{\partial x_i}}=0,$$

$$\overline{\frac{\partial^2\phi}{\partial x_i^2}}=\frac{2}{3}\left(\frac{1}{2}\frac{d^2\phi}{da^2}+\frac{1}{a}\frac{d\phi}{da}\right).$$

Then

$$\bar{\phi}=\phi(a^1)=\sum_i^3\frac{1}{2}\left[\frac{2}{3}\left(\frac{1}{2}\frac{d^2\phi}{da^2}+\frac{1}{a}\frac{d\phi}{da}\right)\right]_{a^1}dx_i^2,$$

since the average of a sum is the sum of the individual averages. Defining

$$\sum_i dx_i^2=da^2 \text{ as } r^2,$$

$$\bar{\phi}=\phi(a^1)+\frac{1}{2}\left[\frac{2}{3}\left(\frac{1}{2}\frac{d^2\phi}{da^2}+\frac{1}{a}\frac{d\phi}{da}\right)\right]_{a^1}r^2.$$

When $\bar{\phi}$ is multiplied by $\frac{1}{2}$ the number of nearest neighbors, C, there is obtained

$$U=U_0+\frac{1}{2}\left[\frac{2}{3}\left(\frac{1}{2}\frac{d^2U_0}{da^2}+\frac{1}{a}\frac{dU_0}{da}\right)\right]r^2.$$

Now if U is expanded as a function of r

$$U=U_0+\tfrac{1}{2}(d^2U/dr^2)_0r^2,$$

it will be seen that

$$\frac{1}{2}\left(\frac{d^2U}{dr^2}\right)_0=2\pi^2m\nu^2$$
$$=\frac{1}{2}\left[\frac{2}{3}\left(\frac{1}{2}\frac{d^2U_0}{da^2}+\frac{1}{a}\frac{dU_0}{da}\right)\right],$$

which is identical with Eq. (18).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 4 APRIL, 1945

Molecular Theory of the Scattering of Light in Fluids*

BRUNO H. ZIMM**
Department of Chemistry, Columbia University, New York, New York

(Received November 21, 1944)

A molecular theory of the scattering of light by fluids of isotropic molecules is developed, utilizing recent advances in the statistical mechanics of condensed phases. The results are shown to be the same in first approximation as those of the continuous theory based on fluctuations originally proposed by Smoluchowski and Einstein. Higher approximations of the molecular theory are especially applicable to the study of critical opalescence and fluids consisting of very large molecules.

INTRODUCTION

THE theoretical calculation of the intensity of the light scattered by the molecules of a transparent substance is an old problem. Nearly half a century ago, Lord Rayleigh[1] developed the theory of the scattering of light by single isotropic molecules and extended it, with some success, to perfect gases. It was soon found, however, that the intensity of scattering by condensed phases was less than that predicted by the formula by more than one order of magnitude. This effect was rightly attributed to destructive interference between the wave trains scattered from different molecules, but the means of calculating the extent of the interference were not available at that time.

Subsequently the difficulty was elegantly circumvented by Smoluchowski[2] and Einstein,[3] who considered the liquid as a continuous medium troubled by small statistical fluctuations in density. The extent of these fluctuations could be calculated from the macroscopic compressibility of the medium, and the intensity of the scattered light was obtained without discussing the individual molecules at all.

It is now possible, however, as a result of recent advances in statistical mechanics, to obtain the Einstein-Smoluchowski formula from a molecular

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

** Present address, Brooklyn Polytechnic Institute, Brooklyn, New York.

[1] Lord Rayleigh, Phil. Mag. **47**, 375 (1899),

[2] M. Smoluchowski, Ann. d. Phys. **25**, 205 (1908).

[3] A. Einstein, Ann. d. Phys. **33**, 1275 (1910). An error, which introduced a factor of $(\mu^2+2)^2/9$ in the formula (24), is corrected by later authors. See references (7) and (8).

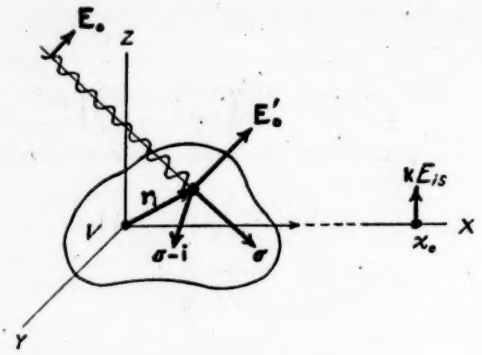

FIG. 1. Geometrical relations between light, system, and observation point.

point of view. The treatment is also applicable in the neighborhood of the critical point, where the Einstein-Smoluchowski method encounters serious difficulties. This molecular development is the subject of the present paper.

FUNDAMENTAL EQUATIONS

We consider a system of N identical molecules, which are smaller than the wave-length of light, in a compact volume V; N, V, and the temperature, are such that the system consists wholly of one fluid phase. (See Fig. 1.) The system is exposed to a train of monochromatic, plane, and plane-polarized light waves whose electric field is given as a function of time and space by the equation:

$$\mathbf{E}(t,\mathbf{r})=\mathbf{E}_0\cos\frac{2\pi}{\lambda}(\boldsymbol{\sigma}\cdot\mathbf{r}-ct), \tag{1}$$

where $\boldsymbol{\sigma}$ is a unit vector in the direction of propagation, λ the wave-length in vacuum, c the velocity in vacuum, and t the time.

In passing through the system, this wave train is modified to

$$\mathbf{E}'(t,\mathbf{r})=\mathbf{E}_0'\cos\frac{2\pi}{\lambda}(\mu\boldsymbol{\sigma}\cdot\mathbf{r}-ct), \tag{2}$$

where μ is the refractive index of the system and $\mathbf{E}'$, the "effective" field, is in general different from $\mathbf{E}$ in magnitude and direction. In each of the molecules of the system, the effective field induces a dipole moment $\mathbf{p}(t,\mathbf{r})$:

$$\mathbf{p}(t,\mathbf{r})=\boldsymbol{\alpha}\cdot\mathbf{E}'(t,\mathbf{r})=\boldsymbol{\alpha}\cdot\mathbf{E}_0'\cos\frac{2\pi}{\lambda}(\mu\boldsymbol{\sigma}\cdot\mathbf{r}-ct). \tag{3}$$

The polarizability tensor, $\boldsymbol{\alpha}$, is a molecular constant. We shall discuss in this paper only the case in which the molecules are isotropic; that is, where $\boldsymbol{\alpha}$ may be adequately represented by a scalar. In addition, we shall not concern ourselves with variations in the value of $\mathbf{E}_0'$ from point to point in the system, but shall assume it constant. The first restriction is for convenience only, to avoid an unduly cumbersome result; the second is forced upon us by the present lack of a complete theory of the effective field $\mathbf{E}'$.

Under these restrictions $\mathbf{p}$ is the same as the average moment per molecule, $\bar{\mathbf{p}}$, of a part of the system containing many molecules, but in which the value of $\boldsymbol{\sigma}\cdot\mathbf{r}$ does not change appreciably, which is known to be

$$\bar{\mathbf{p}}(t,\mathbf{r})=\bar{\alpha}\mathbf{E}(t,\mathbf{r})=\frac{(\mu^2-1)V\mathbf{E}_0}{4\pi N}\cos\frac{2\pi}{\lambda}(\boldsymbol{\sigma}\cdot\mathbf{r}\mu-ct). \tag{4}$$

Here $\bar{\alpha}=[(\mu^2-1)V/4\pi N]$ is the average polarizability per molecule of the system to the external field, $\mathbf{E}$.

The light scattered by the system is observed at a point on the x-axis, x_0, with the distance x_0 large compared to $V^{\frac{1}{3}}$. Observation is made through an analyzer which only transmits light polarized in the z-direction.

Consider a molecule, small compared to λ, located within V at $\mathbf{r}_i=\mathbf{i}x_i+\mathbf{j}y_i+\mathbf{k}z_i$. If $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the usual unit vectors in the x, y, and z directions, the z-component of the electric field, measured at x_0, of the light scattered by this molecule is given by[4]

$$E_{is}=\frac{1}{x_0c^2}\mathbf{k}\cdot\left\{\mathbf{i}\times\left[\mathbf{i}\times\frac{\partial^2}{\partial t^2}\mathbf{p}\left(t-\frac{\mu(x_0-x)}{c},\mathbf{r}_i\right)\right]\right\}$$
$$=\frac{\pi(\mathbf{E}_0\cdot\mathbf{k})(\mu^2-1)V}{x_0N\lambda^2}\cos\frac{2\pi}{\lambda}\times[\mu(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_i+\mu x_0-ct]. \tag{5}$$

The z-component of the electric field, E_s, of the total light scattered by all the molecules is the sum of their individual contributions:

$$E_s=\sum_i E_{is}. \tag{6}$$

[4] M. Born, *Optik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1933), Chap. VII, Sec. 81.

The intensity of the scattered light, I_s, is the time average (over an integral number of cycles) of the square of E_s. The integral over time may be performed immediately; and the constant x_0 may be eliminated in the process:

$$I_s=\left[\frac{\pi(\mathbf{E}_0\cdot\mathbf{k})(\mu^2-1)V}{x_0N\lambda^2}\right]^2\frac{1}{t'}\oint_0^{t'}dt\sum_i\sum_j\cos\frac{2\pi}{\lambda}\times[(\sigma-\mathbf{i})\cdot\mathbf{r}_i\mu+\mu x_0-ct]\cdot\cos\frac{2\pi}{\lambda}[(\sigma-\mathbf{i})\cdot\mathbf{r}_j\mu+\mu x_0-ct]$$

$$=\left[\frac{\pi(\mathbf{E}_0\cdot\mathbf{k})(\mu^2-1)V}{x_0N\lambda^2}\right]^2\left\{\sum_i\cos^2\frac{2\pi\mu}{\lambda}(\sigma-\mathbf{i})\cdot\mathbf{r}_i+2\sum_{i>j}\sum'\cos\frac{2\pi\mu}{\lambda}(\sigma-\mathbf{i})\cdot\mathbf{r}_i\cos\frac{2\pi\mu}{\lambda}(\sigma-\mathbf{i})\cdot\mathbf{r}_j\right\}. \quad (7)$$

The sums in (7) may be expressed and evaluated as integrals, provided certain distribution functions giving the probability of occurrence of specified values of the $\mathbf{r}_i$ are known. The successful use of these functions is the kernel of this paper, and is possible only because of recent advances in the statistical mechanics of condensed systems.*

Mathematically, the argument is this: the sum of a function, $f(\mathbf{r})$, over a large number of discrete values of the independent variable, $\mathbf{r}_1$, $\mathbf{r}_2$, $\cdots$, etc. may be expressed as an integral over $\mathbf{r}$ provided the number of discrete values occurring in the interval between $\mathbf{r}$ and $\mathbf{r}+d\mathbf{r}$ is known. This latter number is the probability of a value between $\mathbf{r}$ and $\mathbf{r}+dr$, and is represented in the notation used by J. E. Mayer[5,6] as $(N/V)F_1(\mathbf{r})$.

$$\sum_i f(\mathbf{r}_i)=\frac{N}{V}\int_V F_1(\mathbf{r})f(\mathbf{r})d\mathbf{r}. \quad (8)$$

A similar theorem holds for double sums:

$$\sum_{i>j}\sum f(\mathbf{r}_i)f(\mathbf{r}_j)=\frac{N(N-1)}{2V^2}\times\int_V\int F_2(\mathbf{r}_1,\mathbf{r}_2)f(\mathbf{r}_1)f(\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \quad (9)$$

Here $[N(N-1)/2V^2]F_2(\mathbf{r}_1,\mathbf{r}_2)$ is the probability of the simultaneous occurrence of a value of both coordinates between $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_1+d\mathbf{r}_1$, $\mathbf{r}_2+d\mathbf{r}_2$.

DISTRIBUTION FUNCTIONS

The distribution functions of the coordinates of the molecules, $(N/V)F_1(\mathbf{r})$ and $[N(N-1)/2V^2]F_2(\mathbf{r}_1,\mathbf{r}_2)$, already defined in terms of probabilities, are so normalized that their average values in the coordinate space are respectively the number and number of pairs of molecules:

$$\int_V\left(\frac{N}{V}\right)F_1(\mathbf{r})d\mathbf{r}=N. \quad (10)$$

$$\int_V\int\frac{N(N-1)}{2V^2}F_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2=\frac{N(N-1)}{2}. \quad (11)$$

For fluids, where long range order is absent, $F_1(\mathbf{r})$ is a constant, equal to unity, and $F_2(\mathbf{r}_1,\mathbf{r}_2)$ is a function only of the relative values of $\mathbf{r}_1$ and $\mathbf{r}_2$, that is:

$$F_2(\mathbf{r}_1,\mathbf{r}_2)=F_2(\mathbf{r}_{12}), \quad (12)$$

where $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$ is introduced.

For the same reason, $F_2(\mathbf{r}_{12})$ approaches a constant when $\mathbf{r}_{12}$ becomes large. Another useful function is then defined by

$$g_2(\mathbf{r}_{12})=F_2(\mathbf{r}_{12})-\lim_{\mathbf{r}_{12}\to\infty}F_2(\mathbf{r}_{12}). \quad (13)$$

The integral, divided by twice the volume, of $g_2(\mathbf{r}_{12})$ over the coordinates of the two molecules is a constant, written as b_2:

$$b_2=\frac{1}{2V}\int\int g_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2=\frac{1}{2}\int g_2(\mathbf{r}_{12})d\mathbf{r}_{12}. \quad (14)$$

The second half of the equation follows from (12).

---

* A treatment of the problem in terms of a continuous rather than a molecular theory, which, however, makes use of the radial distribution function, has been given by L. S. Ornstein and F. Zernicke, Physik. Zeits. **27**, 261 (1926).

[5] J. E. Mayer and E. Montroll, J. Chem. Phys. **9**, 2 (1941).

[6] J. E. Mayer, J. Chem. Phys. **10**, 629 (1942).

EVALUATION OF I_s

In the present case, the $f(\mathbf{r})$ of Eqs. (8) and (9) is $\sin(2\pi\mu/\lambda)(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}$. Using this, the sums in Eq. (7) may be changed to integrals

$$I_s=\left[\frac{\pi(\mathbf{E}_0\cdot\mathbf{k})(\mu^2-1)V}{x_0N\lambda^2}\right]^2 \times\left\{\frac{N}{V}\int F_1(\mathbf{r})\cos^2\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}d\mathbf{r} +\frac{N(N-1)}{V^2}\int\int F_2(\mathbf{r}_1,\mathbf{r}_2)\cos\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i}) \cdot\mathbf{r}_1\cos\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_2d\mathbf{r}_1d\mathbf{r}_2\right\}. \quad (15)$$

Since $F_1(\mathbf{r})=1$, the first term is merely $N/2$, if edge effects be neglected.

$$\frac{N}{V}\int_V F_1(\mathbf{r})\cos^2\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}d\mathbf{r}=\frac{N}{2}. \quad (16)$$

The evaluation of the second term is less trivial. Writing $\mathbf{r}_1$ in terms of $\mathbf{r}_1$ and $\mathbf{r}_{12}$ so that $\mathbf{r}_2=\mathbf{r}_1+\mathbf{r}_{12}$, $d\mathbf{r}_1d\mathbf{r}_2=d\mathbf{r}_1d\mathbf{r}_{12}$, we can write the integral as

$$\frac{N(N-1)}{V^2}\int_V\int F_2(\mathbf{r}_{12})\cos\frac{2\pi\mu}{\lambda} \times(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_1\cos\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_{12}d\mathbf{r}_1d\mathbf{r}_{12}. \quad (17)$$

This may be integrated over $\mathbf{r}_1$, if the second cosine is rewritten in terms of products of cosines and sines of $\mathbf{r}_1$ and $\mathbf{r}_{12}$; the integral over $\mathbf{r}_1$ of terms containing a cosine or sine of $\mathbf{r}_1$ to the first power is zero, and to the second power is $V/2$, so that (17) becomes

$$\frac{N(N-1)}{2V}\int F_2(\mathbf{r}_{12})\cos\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_{12}d\mathbf{r}_{12}. \quad (18)$$

A form more convenient for our purpose, is obtained by using (13) for $F_2(\mathbf{r}_{12})$. If, as usual we neglect edge effects,** the integral of $\cos(2\pi\mu/\lambda)(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_{12}d\mathbf{r}_{12}$ over V is zero and the cross term finally becomes

$$\frac{N(N-1)}{2V}\int g_2(\mathbf{r}_{12})\cos\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_{12}d\mathbf{r}_{12}. \quad (19)$$

In the commonly met special case in which the Einstein-Smoluchowski treatment is useful, the integral (19) may be still further simplified. It may be seen from (13) that $g_2(\mathbf{r}_{12})$ becomes zero when $\mathbf{r}_{12}$ is large. Indeed, for ordinary fluids not in the vicinity of the critical point, it is well known that $g_2(\mathbf{r}_{12})$ is only different from zero at values of $\mathbf{r}_{12}$ less than several molecular diameters. If the molecules are small, $\cos(2\pi\mu/\lambda)(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_{12}$ may be replaced by unity within this region, and (19) becomes simply b_2/V:

$$\frac{1}{2V}\int g_2(\mathbf{r}_{12})d\mathbf{r}_{12}=\frac{b_2}{V}. \quad (20)$$

A value for b_2, involving no significant approximations, has been recently obtained by Mayer.[6] The derivation is too long to repeat here, but, from a generalized form of the grand partition function, he was able to arrive directly at the value***

$$b_2=-\frac{z^2V^2}{2N^2kT}\left(\frac{\partial^2p}{\partial z^2}\right)_T, \quad (21)$$

where z is the fugacity of the substance, normalized in terms of molecules per unit volume, and p is the pressure. By making use of the thermodynamic equation

$$(\partial p/\partial z)_T=NkT/zV, \quad (22)$$

we can transform (21) to the more usable form

$$b_2=-\frac{1}{2}\left[kT\left(\frac{\partial\ln V}{\partial p}\right)_T+\frac{V}{N}\right]. \quad (23)$$

** This neglect may be justified by writing out the limits of both integrals in Eq. (16), and noting that the contribution to the integral of the surface is negligible.

*** The $F_2(\mathbf{r}_{12})$ used here differs from that employed by Mayer in reference (6), in that the latter defines his $F_2(\mathbf{r}_{12})$ over an infinite system, whereas ours is defined over a finite system. In Mayer's case, $\lim_{r_{12}\to\infty}F_2(\mathbf{r}_{12})=1$, but in our case for molecules of finite size, the limit differs from unity by a term of the order of magnitude of $1/N$. Nevertheless, the $g_2(\mathbf{r}_{12})$ and b_2 as defined by (13) and (14) are identical with those used by Mayer.

It should be noted that the only approximations involved in (21) and (23) are those inherent in the fundamental theorems of the semi-classical statistical mechanics.

If we now use (16) and (23) in (15), and overlook the truly negligible difference between N and $N-1$, we get the final expression for I_s in the case of fluids of small molecules not near the critical point as

$$I_s=\frac{\pi^2(\mathbf{E}_0\cdot\mathbf{k})^2(\mu^2-1)^2kTV}{2x_0^2\lambda^4}\left(-\frac{\partial \ln V}{\partial p}\right)_T. \quad (24)$$

A useful related quantity is the "turbidity," τ, the extinction coefficient in Lambert's law,

$$I=I_0e^{-\tau l}. \quad (25)$$

It may also be defined as the total intensity scattered per unit volume divided by the incident intensity, $I_0=\frac{1}{2}E_0^2$. Integration of (24) over all angles of the direction of the primary light (the details are given by Born[4]) yields

$$\tau=\frac{8\pi^3(\mu^2-1)^2kT}{3\lambda^4}\left(-\frac{\partial \ln V}{\partial p}\right)_T. \quad (26)$$

This formula is in complete agreement with that derived by the usual Einstein-Smoluchowski methods.[7,8]

[7] S. Bhagavantam, *The Scattering of Light and Raman Effect* (Andhra University, Waltair, India, 1940).
[8] J. Cabannes, *La Diffusion Moléculaire de la Lumière* (Les Presses Universitaires de France, Paris, 1929).

CONCLUSION

In general, the approximation of replacing the cosine by unity in (19) will not be valid. In the neighborhood of the critical point, for example, or for fluids or glasses composed of very large molecules, $g_2(\mathbf{r}_{12})$ will not fall to zero at values of $\mathbf{r}_{12}$ less than the wave-length of light, and here use must be made of the complete form (19) rather than (20). The expression for I_s then is

$$I_s=\frac{\pi^2(\mathbf{E}_0\cdot\mathbf{k})^2(\mu^2-1)^2V}{2x_0\lambda^4}$$
$$\times\left\{\frac{V}{N}+\int_V g_2(\mathbf{r}_{12})\cos\frac{2\pi\mu}{\lambda}(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}_{12}d\mathbf{r}_{12}\right\}. \quad (27)$$

The first term is just the light scattered by N isolated molecules, while the second term describes the interference resulting from correlations in position of the molecules. It will be noted that the second term is essentially the Fourier transform, as a function of the angles between illumination and observation, of $g_2(\mathbf{r}_{12})$, in close analogy to the well known formulas for the scattering of X-rays.

The extension of this method to many-component systems is straight-forward and will be reported in a later paper.

ACKNOWLEDGMENT

The author is indebted to Dr. J. E. Mayer for helpful discussion and advice.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 4 APRIL, 1945

Potentiometric Determinations of H-Ion Concentration in Hydrocarbon Oils

ANDREW GEMANT
The Detroit Edison Company, Detroit, Michigan
(Received January 18, 1945)

The paper discusses potentiometric measurements of hydrogen ion concentration carried out in hydrocarbon oils that have attained high electrical conductivity (a) through oxidation in the laboratory, (b) through deterioration in service, (c) through addition of certain compounds. The e.m.f. data are interpreted by comparing them with those obtained from lauryl sulfonic acid solutions in oil. The results indicate that the hydrogen ion concentration in the three types of oils is too low to account for the total observed electrical conductivity. It is obvious, then, that the predominant mechanism of ion generation is different from the usual acidic dissociation. A bimolecular reaction leading to two organic ions is suggested on the basis of evidence from organic chemistry and a quantitative relation that follows from conductivity data presented in this paper.

1. THE PROBLEM

IN a previous publication[1] the author showed that hydrogen ion concentration can be measured in dielectric liquids with a dielectric constant as low as 2.3, which is the usual order of magnitude in insulating liquids. The liquids previously investigated were xylene and dioxane. The author believes that, in the future, electrochemical measurements, not only with glass, but with other electrodes, will be as common in the realm of dielectric liquids as they are today in the domain of aqueous solutions. The purpose of the present paper is to show the application of the method to the field of electrical insulating oils, and to the investigation of their deterioration in service.

During oxidation of an insulating oil, its electrical conductivity increases, and this is one of the chief reasons that an oxidized oil is considered objectionable. In the course of the oxidation various oxidation products, including acids, are formed. It is generally recognized that the increase in conductivity and the formation of acid are in some way related; in fact, the degree of oxidation is often estimated by the total acidity, or so-called acid number. While this point of view is certainly correct in a qualitative sense, the mechanism of this relationship has not yet been definitely established.

One fact is certain: whenever the conductivity is independent of frequency (and this is very often the case), the conductivity is not due to rotation of dipolar groups, but to the migration of ions. It is entirely unknown as yet, however, by what mechanism these ions are generated, and what their chemical constitution is. Referring to the statement made above, all one can say is that these ions are probably a product of the acids that are the result of oxidation. Lacking any positive knowledge in this matter, most writers working in this field assume, either implicitly or explicitly, that the acids formed (or, if metals were present during deterioration, their salts) are electrolytically dissociated. Among the authors stating this view, J. B. Whitehead,[2] J. C. Balsbaugh,[3] and the present writer[4] may be quoted. J. D. Piper[5] assumes electrolytic dissociation at the boundary of colloidal particle and solvent, and unequal distribution, between the solvent and particle, of the positive and negative ions formed.

It was thought that use of the e.m.f. method, with glass electrodes, could throw some light on this problem. If dissociation of acids, in the usual sense, takes place in oxidized oils, there must be a hydrogen ion concentration corresponding to the electrical conductivity, since the latter would then be due to the presence of both organic anions and hydrogen ions. The method at hand allows a direct check as to whether or

[1] Andrew Gemant, J. Chem. Phys. **12**, 79 (1944).

[2] J. B. Whitehead and F. E. Mauritz, Elec. Eng. **56**, 465 (1937).

[3] J. C. Balsbaugh, A. A. Assaf, and J. L. Oncley, Ind. Eng. Chem. **34**, 92 (1942).

[4] Andrew Gemant, *Liquid Dielectrics* (John Wiley and Sons, Inc., New York, 1933), p. 61.

[5] Joseph Sticher and J. D .Piper, Ind. Eng. Chem. **33**, 1567 (1941).

not this is the case. Whichever answer is obtained, it will help in narrowing the range in which the complete solution of the problem will be found.

2. SOLUTIONS OF LAURYL SULFONIC ACID IN XYLENE

In the solutions investigated during the course of the previous work on this subject, hydrocarbon oil was not used as the solvent. Before examining oxidized oils, it was necessary to study a system with an oil as the solvent in which a definite hydrogen ion concentration was established. Toluene sulfonic acid and picric acid used in the low molecular weight solvents are not soluble in oils. Piper[6] found that lauryl sulfonic acid is reasonably soluble in paraffin oil and gives conductivities significantly higher than that of the oil. This acid was used in the present investigation. Because lauryl sulfonic acid as the solute was not included in the previous work, the first step was to examine solutions of it in a low molecular weight hydrocarbon, xylene, in order to establish continuity with previous results. Because of the relative chemical instability of lauryl sulfonic acid, the results are less reproducible than those obtained with toluene sulfonic acid.

Figure 1 shows the cell used for e.m.f. measurements which embodies several improvements over cells used previously in this study. *A* and *B*

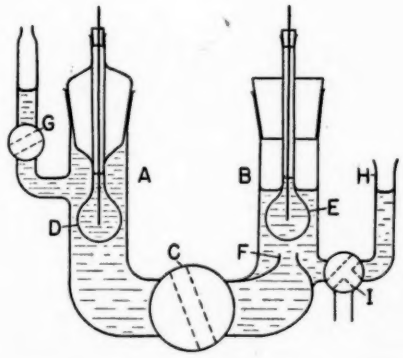

FIG. 1. Diagram of glass cell for e.m.f. measurements.

are the two half-cells; *A* contains a standard solution of relatively high conductivity and density which fills the right-hand extension of *A* up to the opening *F*, *B* contains the solution to be measured. *C* is a large-bore stopcock, and *D* and *E* are the glass electrodes. The stopper that supports *D* is made of ground glass to fit the opening of *A*, the stopper for *E* is paraffinized

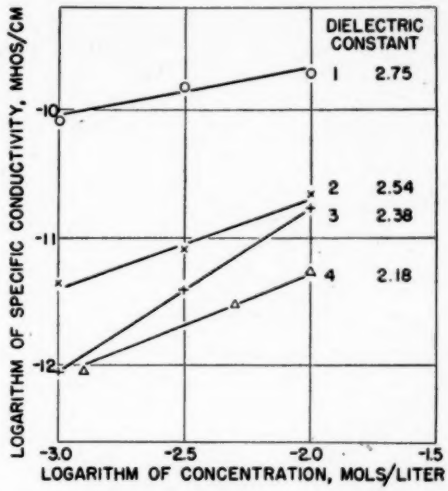

FIG. 2. Specific conductivity *vs.* concentration for lauryl sulfonic acid solutions. Solvent for Curves 1, 2, 3—xylene, for 4—hydrocarbon oil.

cork. With stopcock *C* closed, *A* is completely (or nearly so) filled with the standard solution through stopcock *G*. The sample is introduced at the opening *H*; since the standard solution is made to have a higher density, no turbulent mixing will take place at *F*. During the measurement *C* is open; when the measurement is completed, *C* is closed and the sample is drained out by using the three-way stopcock, *I*, and the cell is ready for another solution. After two or three measurements, the liquid surface of *F* is renewed by carefully opening *C* and *G* to allow a small amount of liquid to pass.

For the standard solution an addition of about 3 percent of ethyl alcohol and 6 percent of carbon tetrachloride to the solvent used in half-cell B is suitable. This increases the conductivity to the required level of 10^{-10} mho/cm and also provides the necessary density differential. It is best to use the same solute as that present in *B* in a concentration of 0.01 or 0.02 normal. When the solvent of the sample was mineral oil, the necessary high conductivity could not be obtained; in this case xylene was used in the standard. Also, when oxidized oils were tested

[6] J. D. Piper, A. G. Fleiger, C. C. Smith, and N. A. Kerstein, Ind. Eng. Chem. **34**, 1505 (1942).

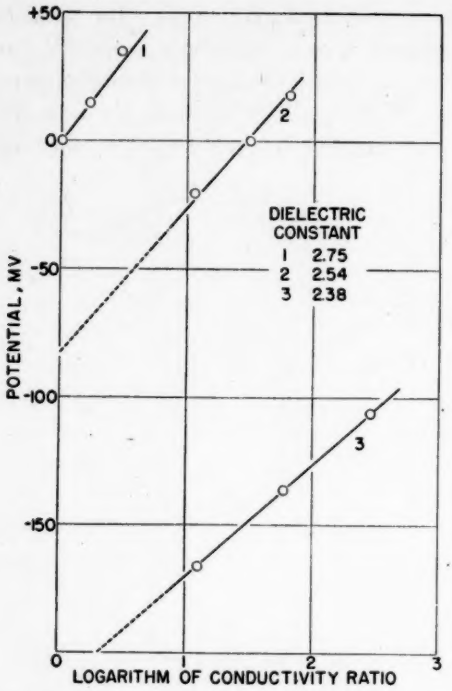

FIG. 3. E.m.f. *vs.* conductivity ratio for lauryl sulfonic acid solutions in xylene.

in B, the electrolytes in both half-cells were by necessity different; in this case toluene sulfonic acid or lauryl sulfonic acid was used in the standard half-cell. It is obvious that such a cell does not represent a concentration cell and would not be suited for a rigorous quantitative study. For the semi-quantitative problem at hand, the use of such a cell was deemed justified.

The solutions investigated first were of lauryl sulfonic acid in xylene. By means of additions of ethyl alcohol, three solvents of dielectric constants 2.75, 2.54, and 2.38, variously, were obtained. The concentration of the acid ranged from 10^{-3} to 10^{-2} normal. The specific conductivity is shown in Fig. 2 on a bilogarithmic scale, Curves 1, 2, and 3. The slope of the three curves is respectively 0.4, 0.7, and 1.3. From the mass action law it follows[1] that

$$\sigma=(10^{-3}\Lambda_0\sqrt{K})\sqrt{c}, \qquad (1)$$

in which σ = specific conductivity, Λ_0 = equivalent conductivity, K = dissociation constant, c = molar concentration. This equation implies a slope of 0.5. The gradual increase of the slope beyond the value 0.5 is in agreement with observations in the previous paper and also in papers of Fuoss and Kraus.[7]

The e.m.f. data are assembled in Fig. 3, the abscissa being the logarithm of the ratio of the conductivities in the two half-cells. For this case an approximate theoretical equation was shown[1] to hold, namely

$$E=118(1-t_H)\log_{10}(\sigma_A/\sigma_B)+(1.55\times10^{-4}/b)(1-t_H)(1/D_A-1/D_B), \qquad (2)$$

in which E = e.m.f. in mv, t_H = hydrogen transference number, σ_A and σ_B = specific conductivities of solutions in A and B, D_A and D_B = dielectric constants of solutions in A and B. The value of b is given by $1/b=1/r_c+1/r_a$, in which r_c = radius of cation, and r_a = radius of anion in cm. The data for t_H and b as computed from the experimental results are shown in Table I. The figures were obtained from the e.m.f. data; t_H from the slopes and b from the intercepts of the curves in Fig. 3. The values for t_H and b are both of the correct order of magnitude, showing a slight dependence on the dielectric constant.

In these solutions, therefore, the e.m.f. is a function of conductivity, in exactly the same way as is to be expected from the reasonable assumption that the conductivity is due to a dissociation of the acid into hydrogen ion and anion.

Before proceeding to test the same acid in hydrocarbon oil as solvent, it was necessary to decide in which way to take account of the rather different viscosities in the two half-cells. Because of the relation for the H^+ ion concentration:

$$[H^+]=(10^3/\Lambda_0)\sigma, \qquad (3)$$

TABLE I.

D_B	t_H	b, cm
2.75	0.46	*
2.54	0.51	2.8×10^{-8}
2.38	0.63	2.1×10^{-8}

* Since D_A was also 2.75, it was not possible to compute b in this case.

the ratio of conductivities in Eq. (2) can be used only if the equivalent conductivities, Λ_0, are equal or nearly so. If this is not the case, the

[7] R. M. Fuoss and C. Kraus, J. Am. Chem. Soc. **55**, 1019 (1933).

first term in Eq. (2) should read:

$$118(1-t_H)\log_{10}(\sigma_A\Lambda_{0B}/\sigma_B\Lambda_{0A}), \qquad (4)$$

or, if it is assumed that Λ_0 is inversely proportional to the viscosity η, and that the influence of other specific factors may be disregarded in first approximation:

$$118(1-t_H)\log_{10}(\sigma_A\eta_A/\sigma_B\eta_B). \qquad (5)$$

Theoretically the term (5) should be preferable to the form given in Eq. (2), if the two viscosities differ. An attempt was made to decide experimentally between the two formulas by using the e.m.f. method. A solvent was prepared containing 6.7 percent polystyrene in xylene. This had a viscosity at 25°C of 0.31 poise, whereas that of the xylene was 0.0059. Two solutions of lauryl sulfonic acid (10^{-2} and 3×10^{-3}) were prepared in this solvent and the e.m.f. measured against the standard solution of lauryl sulfonic acid. The data are plotted on Fig. 4 which also contains Curve 3 of Fig. 3 for comparison. The two points as plotted using the term (5) are indicated by ⊗; plotted using Eq. (2), without viscosity correction, by ○. The former points fit the extension of the line better than the latter. Thus, experimental evidence, in favor of the use of the viscosity correction, was obtained. More work along similar lines should be carried out in order to clarify further this important question. This is, by the way, an example that shows the possible uses of the e.m.f. method in the field of liquid dielectrics.

3. LAURYL SULFONIC ACID IN HYDROCARBON OIL

In this section the results obtained on lauryl sulfonic acid solutions in a hydrocarbon oil will be reviewed. The mineral oil, which was a typical transformer oil, had the following characteristics (Table II). The oil was dried for a few hours at 120°C before use.

TABLE II.

Density, g/cm³	0.87
Viscosity at 25°C, poise	0.14
Flash point, C	146
Pour point, C	−50
Acidity, mg KOH/g	0.005
Elec. conductivity at 25°C, mho/cm	1×10^{-14}
Dielectric constant	2.18

The conductivity data are shown as Curve 4 of Fig. 2. Its slope is 0.8, somewhat larger than that characteristic of typical dissociation, but its location with respect to the three curves referring to xylene solutions of higher dielectric constant shows that there is no break in the behavior of dielectric solutions down to a dielectric constant as low as 2.18. This is in keeping with the author's idea of extending the e.m.f. method, so

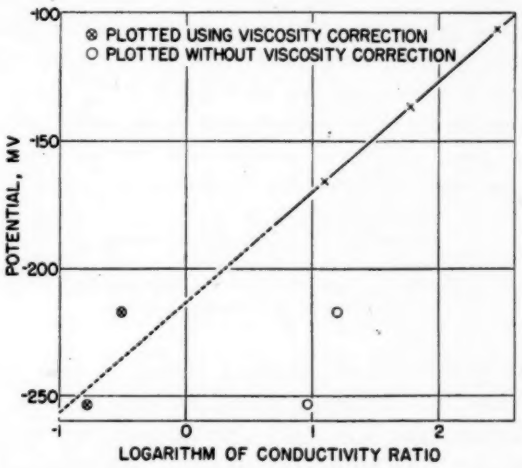

FIG. 4. E.m.f. *vs.* conductivity ratio for lauryl sulfonic acid in xylene plus polystyrene.

useful in highly conducting solutions, into the field of dielectrics.

Data on e.m.f. are given in Fig. 5, the abscissae containing the viscosity correction. Dilutions from three different stock solutions are shown by different markings. The reproducibility of the data on these solutions is limited by the noticeable chemical instability of the acid, particularly in the presence of traces of moisture. In keeping with the general trend of this series of investigations, no attempt was made to work under conditions of extreme dryness of the solutions tested.

The intercept of the line with the ordinate axis is −45 mv. From this figure a value of b, the average ionic radius, can be deduced, using Eq. (2) and taking $t_H=0.5$ (the value for the standard solution). D_A is 2.6 and D_B is 2.2. Hence, $b=12A$ units is obtained, five times as large as in xylene. Realizing that ions always carry molecules of solvation, the larger radius in oil, as compared with that in xylene, will be understandable.

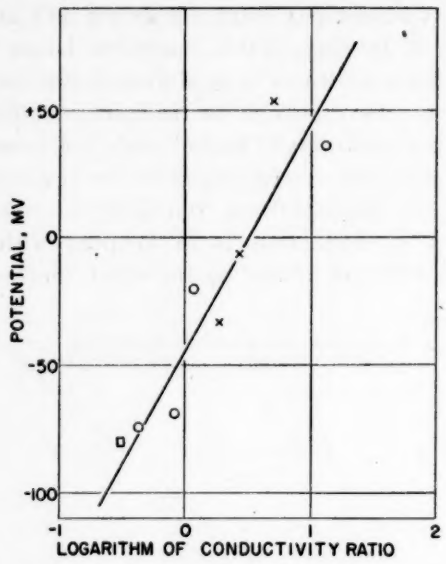

FIG. 5. E.m.f. *vs.* conductivity ratio for lauryl sulfonic acid solutions in hydrocarbon oil.

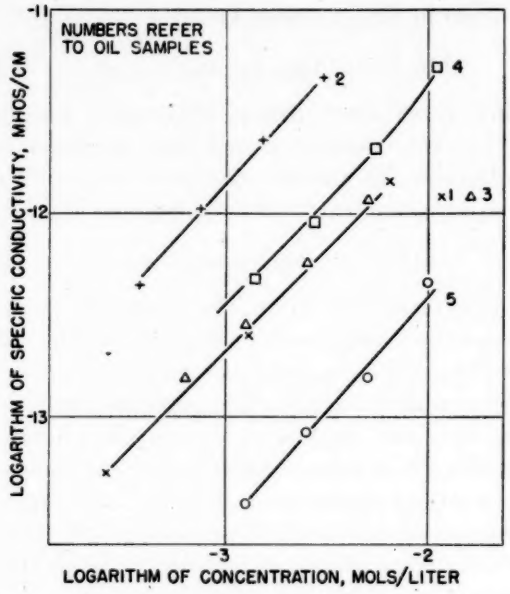

FIG. 6. Specific conductivity *vs.* concentration of acid for oxidized hydrocarbon oils. (Samples listed in Table III.)

It should be emphasized, however, that the cell used for obtaining the data of Fig. 5 is not a concentration cell, since the solvents are quite different. The intercept, therefore, will contain a specific term, not covered by Eq. (2) which latter accounts only for the differences in dielectric constants. In spite of its limitations, the curve of Fig. 5 will serve as a basis for the interpretation of data on oxidized oils given in the next section. Figure 5 shows the e.m.f. *vs.* conductivity relation for a hydrocarbon oil in which the total conductivity is essentially due to the presence of electrolytic dissociation products of an acid—hydrogen ions and corresponding anions.

4. OXIDIZED HYDROCARBON OILS

The results obtained up to this point permit an attack upon the problem outlined at the outset. In order to test oxidized mineral oils, five different samples were used. Four of these were transformer oils, deteriorated in service. The fifth sample was the same oil as that used in the preceding section, oxidized in the laboratory at 150°C in the presence of copper as catalyst, and under free access of air. Table III gives the acidities of the five samples in question.

Figure 6 shows the electrical conductivity as a function of concentration of the acid in mols/liter, as usual. The various dilutions were prepared by means of the pure mineral oil mentioned before. The conductivities, measured with a.c. voltage ranging between frequencies of 100 and 10,000 cycles, were independent of the frequency, thus indicating ionic conduction mechanism.

Two conclusions can be drawn from Fig. 6:

(1) The range of conductivities (10^{-13} to 10^{-11}), corresponding to molar acid concentrations between 10^{-3} and 10^{-2}, is about the same as that for the sulfonic acid solutions in oil (10^{-12} to 10^{-11}). This appears to indicate a similarity between the two cases.

(2) The slopes of the curves are respectively (starting from the top) 1.10, 1.05, 1.05, and 1.12, values that are close to 1.0. In contrast to this, the slopes for the strong acids were near 0.5 in the range of low concentration and decidedly above 1.0 in the range of higher concentrations, as the results in this and the previous publication show. Later in this paper this result will be

TABLE III.

Number of oil sample	Place of deterioration	Acidity in mg KOH/g
1	Transformer in service	0.42
2	Transformer in service	0.18
3	Transformer in service	0.30
4	Transformer in service	1.35
5	Laboratory	0.57

tentatively interpreted from the standpoint of ion generation.

The results of e.m.f. measurements on three of the five specimens are shown in Fig. 7. For comparison, the curve from Fig. 5 is also reproduced. The following points should be mentioned.

(1) The potentials are not as well defined and stable as they were observed to be when sulfonic acid, or picric acid was present. They are unstable and variable, of the type referred to as "floating" or undefined potentials. The unstable potentials are the more significant because the deteriorated oils were chemically rather stable, the conductivities not changing with time. Such floating potentials occur (also in aqueous solution) when the concentration of ions corresponding to the electrode in use is so low that the actual ion concentration at the electrode surface depends on secondary uncontrollable factors.

(2) The trend of the potential with varying dilution does not generally follow the direction characteristic of all previous measurements (increase of e.m.f. with increasing dilution). This again indicates that, if hydrogen ions are generated at all by the acids present, their concentration is too low to control the potential at the glass electrode.

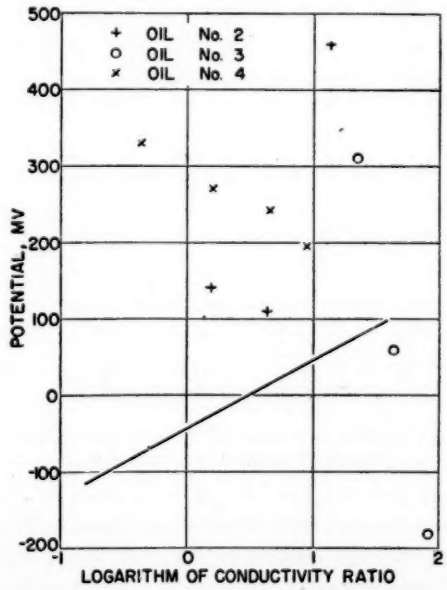

FIG. 7. E.m.f. *vs.* conductivity ratio for oxidized hydrocarbon oils. (Solid line, referring to lauryl sulfonic acid solutions, reproduced from Fig. 5 for comparison.)

(3) The majority of measured points (eight out of ten) is considerably above the curve of comparison, which means that the hydrogen ion concentration is considerably below the total ion concentration. The amount of divergence can be estimated by reading from the extension of the comparison curve the abscissas corresponding to the measured potentials. It can be seen that conductivities due to hydrogen ions are about a hundred to ten thousand times smaller than the total conductivities. In other words, the hydrogen ions—if present at all—are only a small fraction (10^{-4} to 10^{-2}) of the total ions present.

These results are confirmed by a second set of data obtained with solvents of relatively low viscosity: a mixture of xylene and hydrocarbon oil. Two ratios were used, xylene-oil 1:1, and xylene-oil 2:3. Comparison was obtained with solutions of toluene sulfonic acid in these two solvents. The oxidation products were those contained in oil sample No. 1, the solutions being prepared by mixing oil No. 1, pure oil, and xylene in various required proportions. The results are shown in Fig. 8.

These results are similar to those of the pre-

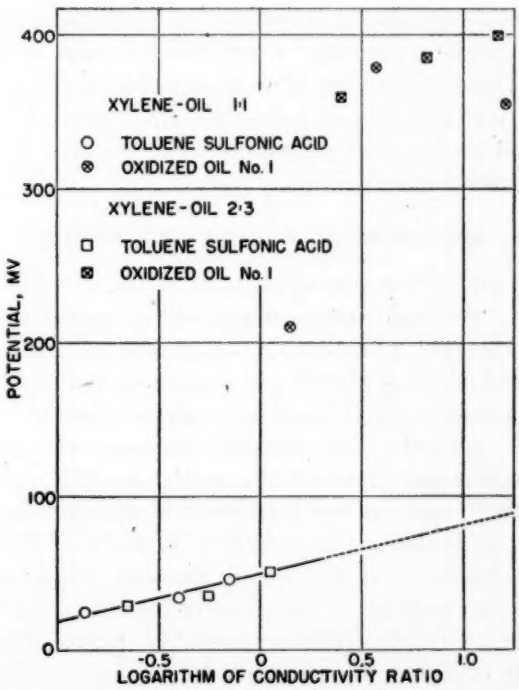

FIG. 8. E.m.f. *vs.* conductivity ratio for mixtures of oxidized oil No. 1 and xylene. (Toluene sulfonic acid solutions in same solvent for comparison.)

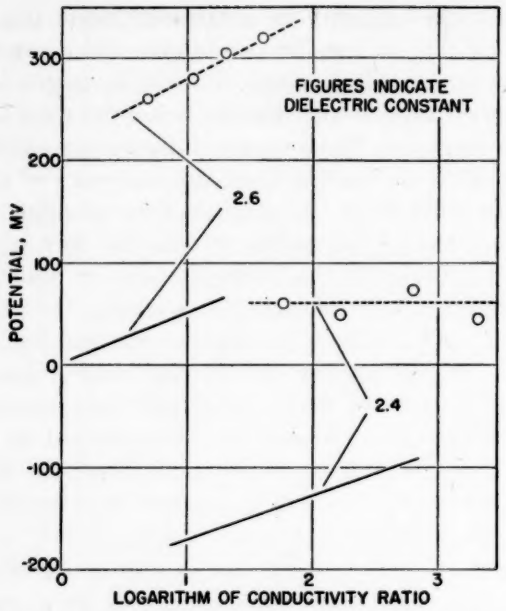

FIG. 9. E.m.f. *vs.* conductivity ratio for solutions of phenol in xylene. (Solid lines refer to lauryl and toluene sulfonic acid solutions.)

vious set. In particular it can be seen that the measured points are located well above the curve obtained by using toluene sulfonic acid as the electrolyte. In carrying out the semi-quantitative estimate as above, by shifting the points to the right until they reach the extension of the line below, again it will be seen that the hydrogen ion concentration is only a small fraction of the total ion content responsible for the high conductivity observed.

5. SOLUTIONS OF PHENOL AND ASPHALT

Two further sets of measurements, substantiating the main results obtained, are reported in this section. These two sets comprise e.m.f. data on solutions of phenol and asphalt in xylene and oil respectively. Phenol was selected because it is a typical weak acid in aqueous solutions (dissociation constant in water at 25°C, 1.3×10^{-10}) and, in this respect at least, represents the acids formed as oxidation products, which, as is known from titration in alcoholic solutions,[8] are also weak acids. Solutions of phenol in xylene have a conductivity appreciably higher than that of xylene alone. Asphalt was selected because it is known to cause high power factors in insulating oils.[6]

The results of the tests involving phenol are shown in Fig. 9. One set (lower part of figure) refers to solutions in xylene (dielectric constant 2.4); for comparison, the curve for lauryl sulfonic acid solution is given. The other set (upper part of figure) refers to xylene-ethyl alcohol ($D=2.6$); the comparison curve is that for solutions containing toluene sulfonic acid. The potentials obtained from phenolic solutions are not so irregular in their trend as those obtained from oxidized oils, but their position is above the lines of comparison. If plotted upon the extension of the lines of comparison, they would indicate hydrogen ion concentrations lower than that corresponding to their conductivity.

The conductivity data for two different brands of asphalt in the oil characterized in Table II are given in Fig. 10, in which the concentrations are expressed in relative units. The slopes, particularly toward lower concentrations, are close to 0.5. It is not clear, however, why these solutions should behave like typical weak electrolytes.

The e.m.f. data for these two solutions are given in Fig. 11. Circles and crosses refer to the same respective solutions as those in Fig. 10. The line of comparison is that for lauryl sulfonic acid. The potentials observed were of the floating type, and, with the exception of two points, are located above the line of comparison. The hydro-

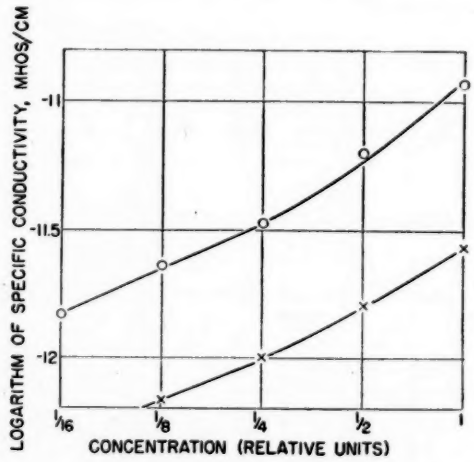

FIG. 10. Specific conductivity *vs.* concentration of two brands of asphalt in mineral oil.

[8] R. N. Evans, and J. E. Davenport, Ind. Eng. Chem. (Anal. Ed.) 9, 321 (1937).

gen ion concentration is certainly only a small fraction of the total ions present.

6. DISCUSSION OF RESULTS. GENERATION OF IONS IN HYDROCARBONS

The experimental results presented in this paper answer, in the negative sense, the question formulated in the introductory section. The hydrogen ion concentration, as measured by the e.m.f. method in oils possessing high conductivities (as a result of deterioration in service, oxidation in the laboratory, or the addition of certain compounds), is too low to account for the total observed electrical conductivity. The conclusion is then inevitable, that the generation of ions from organic molecules present in oils of high conductivity does not take place by a process of typical acidic dissociation into H^+ ions and an anion. If such a process is active at all, the acidic dissociation constant K of the compounds in question is too small to account for the major part of the ionic components present. In the previous publication[1] it was shown that the dissociation constant K of toluene sulfonic acid and picric acid in xylene and dioxane is of the order $10^{-20}-10^{-22}$. Hence, the K of the compounds in question must be several orders of magnitude smaller. The predominant type of dissociation in these solutions must be different from the acidic, and the majority of the positive ions different from H^+ ions.

While a satisfactory answer to this latter problem can be found only by means of experiment, a guiding hypothesis will be developed briefly in the following.

In aqueous and alcoholic solutions, acidic and basic dissociation is predominant, because both the H^+ and OH^- ions have a high energy of solvation. In hydrocarbons, however, acidic dissociation is exceptional, apparently being restricted to the strong organic sulfo and nitro acids. It is probable that, in such solvents, both the positive and the negative ion will be organic groups, and not simple ions such as H^+ and OH^-, because the affinity of an organic ion for the solvent molecules will evidently be greater, and the solvation energy sufficiently large, to compensate for the energy of dissociation. While organic anions are known in great number, organic cations are represented chiefly by the various amines, and there is a great likelihood that it is this type of cations that is present in insulating liquids. Apart from the amines, it is known that organic cations exist in gaseous discharges;[9] they were detected in large number by mass spectroscopy. As examples of such ions, $C_2H_2^+$, $C_2H_4^+$, $C_6H_6^+$, and the like, may be quoted. If such ions exist in a gas phase, their existence in a liquid dielectric is even more probable.

The mechanism of ion formation of this type is not a dissociation, but probably a reaction of two or three molecules, accompanied by electron transfer from one to the other. While the usual dissociation is a monomolecular reaction, the type postulated here is a bimolecular or trimolecular one.*

The conductivity data on oxidized oils (Fig. 6) supply experimental evidence in favor of this statement. If the reaction is $A+B\rightleftarrows C^+ + D^-$,

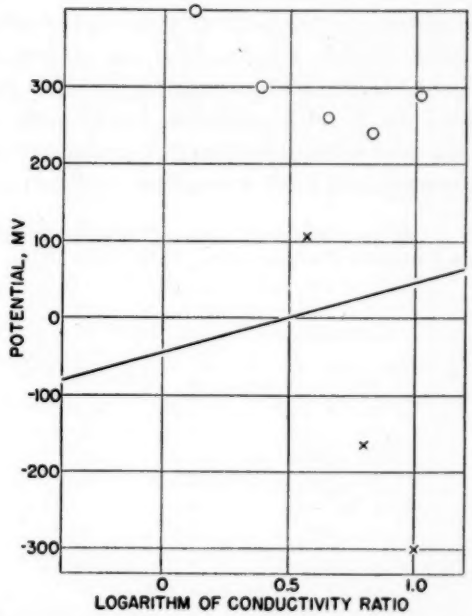

FIG. 11. E.m.f. *vs.* conductivity ratio for solutions of two brands of asphalt in mineral oil. (Solid line refers to lauryl sulfonic acid solutions.)

then the mass action law gives

$$c_A c_B \sim c_C + c_{D^-}, \qquad (6)$$

[9] G. Glockler, and S. C. Lind, *The Electrochemistry of Gases* (John Wiley and Sons, Inc., New York, 1939).

* A continuation of this research now under way seems to substantiate these postulates.

c being respective concentrations. If the oxidized oil is present in a variable concentration, c_0, in an indifferent oil, as was the case in the tests described above, then both c_A and c_B are proportional to c_0. As to c_{C+} and c_{D-}, both are equal and proportional to σ, the electrical conductivity. Hence, from (6)

$$c_0^2 \sim \sigma^2,$$

or

$$c_0 \sim \sigma, \tag{7}$$

instead of Eq. (1), characteristic for dissociation. In logarithmic plotting, the slope in such a case must be unity, and, as may be recalled, this conclusion was well fulfilled in the data shown on Fig. 6.

While the chemical nature of the ions C^+ and D^- could—as has been said—be found only by experiment, two known cases from organic chemistry may be cited to illustrate that the formation of organic cations, apart from cases involving amines, is not purely hypothetical.

One of the cases is that of cyclic hydrocarbons possessing double bonds, such as pinene and camphene. If an acid (usually a halogen acid) is added to $C_{10}H_{16}$, addition compounds like $C_{10}H_{17}X$ are formed. Meerwein has shown[10] that these compounds have a tendency to form positive ions $C_{10}H_{17}^+$. Such ion formation may be assumed to take place to a small degree also in the presence of an organic acid HAc, thus:

$$C_{10}H_{16}+HAc \rightleftarrows C_{10}H_{17}^+ + Ac^-,$$

as an example of the above described general bimolecular reaction.

As another illustration, triphenylcarbinol may be mentioned. As Gomberg and Anderson[11] have shown, the latter is definitely basic in character, leading to the positive ion CPh_3^+. Such a dissociation has been known to take place in the presence of a halogen acid, but the possibility exists that it would also occur in the presence of organic acids; in this case the reaction would read:

$$CPh_3OH+HAc \rightleftarrows CPh_3^+ + Ac^- + H_2O.$$

While it is by no means maintained that the two types of compounds, as here discussed, actually play a role in the generation of ions in hydrocarbon oils, they are cited as evidence from organic chemistry in favor of the mechanism depicted above.

The author wishes to thank his colleagues, A. G. Fleiger and N. A. Kerstein, for cooperation in this research.

[10] W. A. Waters, *Physical Aspects of Organic Chemistry* (D. Van Nostrand Company, Inc., New York, 1937).

[11] L. C. Anderson and W. A. Fisher, J. Am. Chem. Soc. 66, 589 (1944).

The Calculation of the Contribution of Freely Rotating Groups to Electron Scattering by Gases

J. KARLE
Chemistry Department, University of Michigan, Ann Arbor, Michigan
(Received February 19, 1945)

The contribution from freely rotating atoms to the intensity of electron scattering by gaseous molecules is obtained by means of an asymptotic evaluation of an integral, using the saddle point method. It is possible now to estimate the effect of the approximation in using the Debye formula, which is a specialization of the derived series, and, if desired, to obtain a higher degree of accuracy. Two cases are considered numerically.

IN many molecules in the gaseous state internal vibrations of large amplitude and even practically unhindered rotation are possible. This, of course, is well known from heat capacity and spectroscopic investigations. In his paper concerning the effect of various types of internal motion in gaseous molecules on the resulting intensity of scattered electrons, P. Debye[1] made an important contribution to the calculation of the effect of a freely rotating group in a special type of molecule by evaluating the integral

$$\int \frac{\sin sr}{sr} dW, \tag{1}$$

by means of an asymptotic formula. In the integrand, $s=(4\pi/\lambda)\sin(\theta/2)$, r is the varying distance of a rotating atom from another whose position in space is fixed, and which is not on the axis of rotation (for then r would not vary) and dW is the probability of finding the rotating atom in any position on the circle of rotation. s corresponds to sk in Debye's treatment.

It is the purpose of this paper to afford the investigator a means for estimating the effect of the approximation introduced by using the Debye formula and for obtaining a greater accuracy, if desired. The general case, in which there are no restrictions on the molecular parameters, is treated and an expression is derived which is the sum of four asymptotic series. It can then be shown that Debye's formula is obtained if one takes the first term in two of the series, neglecting the other two, and specializes it to Debye's example. By means of these semi-convergent series it is easy to estimate the approximation introduced by using the Debye formula (or, more generally, the formula which is the sum of the first terms in two of the series) and, in addition, higher accuracy may be obtained by including additional terms.

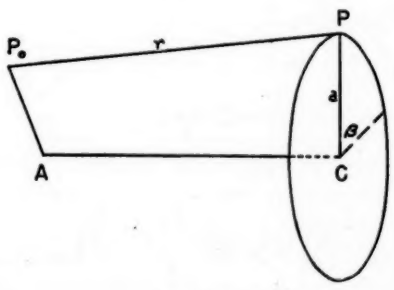

FIG. 1.

MATHEMATICAL DEVELOPMENT

Consider the point, P, rotating with fixed radius of rotation, a, about the axis AC. Its distance, r, from a fixed point in space, P_0, can be shown to be

$$r=(c_1-c_2\cos\beta)^{\frac{1}{2}}, \tag{2}$$

where

$$c_1=(l_2^2+l_1^2)/2, \quad c_2=(l_2^2-l_1^2)/2,$$

and β is the angle of rotation. $r_{max}=l_2$, $r_{min}=l_1$, and, clearly, $\beta=0$ when $r=l_1$.

The contribution to the total scattering function from a pair of atoms at P and P_0, respectively, is given by $(\sin sr)/sr$. It is necessary however to consider the average contribution by the changing distance in the course of a rotation. Thus, we obtain an integral of the form of (1) which is an averaging of the contributions from all positions of orientation. We have by

[1] P. Debye, J. Chem. Phys. 9, 55 (1941).

expressing r as in (2) above,

$$I=\int_0^{2\pi}\frac{\sin\left[x(1-p\cos\beta)^{\frac{1}{2}}\right]d\beta}{x(1-p\cos\beta)^{\frac{1}{2}}2\pi}, \tag{3}$$

where $x=sc_1^{\frac{1}{2}}$, $p=c_2/c_1$ and $d\beta/2\pi=dW$ since, in free rotation, all positions are equally probable and the weight factor as a function of position reduces to unity. Integral (3) is the imaginary part of

$$\frac{1}{\pi x}\int_0^{\pi}\frac{\exp\left[ix(1-p\cos\beta)^{\frac{1}{2}}\right]}{(1-p\cos\beta)^{\frac{1}{2}}}d\beta. \tag{4}$$

This integral will now be evaluated by the saddle point method, the details of which have been clearly presented by Debye.[2] The principle of this method is that integrals of the type in (4) can be evaluated asymptotically by considering the contribution in the vicinity of the extrema of $f(\beta)=(1-p\cos\beta)^{\frac{1}{2}}$, which occur when $\beta=0$ and $\beta=\pi$, the saddle points. The evaluation is accomplished by choosing a contour of integration along a path of steepest descent (steepest decrease of magnitude of the integrand) through the saddle points.

In order to obtain now the contribution from the neighborhood of $\beta=0$, we define a new variable,

$$t=f(\beta)-f(0)=(1-p\cos\beta)^{\frac{1}{2}}-(1-p)^{\frac{1}{2}}. \tag{5}$$

From (5) we get

$$\sin\beta(t)=\frac{2(1-p)^{\frac{1}{4}}}{p^{\frac{1}{2}}}t^{\frac{1}{2}}\left(1-\frac{(2-3p)t}{2p(1-p)^{\frac{1}{2}}}-\frac{t^2}{p}-\frac{t^3}{4p(1-p)^{\frac{1}{2}}}\right)^{\frac{1}{2}}, \tag{6}$$

$$=\frac{2(1-p)^{\frac{1}{4}}}{p^{\frac{1}{2}}}t^{\frac{1}{2}}\Big/\sum_{n=0}^{\infty}b_nt^n.$$

The values of b_0, b_1, b_2, and b_3 are given along with the final expression.

We now use (5) and (6) to express integral (4) as a function of t, and then make an additional change of variable, setting $ixt=-\tau$. This gives

$$I_0\sim\frac{\exp\left[ix(1-p)^{\frac{1}{2}}\right]}{\pi x(-ix)^{\frac{1}{2}}(1-p)^{\frac{1}{4}}p^{\frac{1}{2}}}\int_0^{\infty}\frac{e^{-\tau}}{\tau^{\frac{1}{2}}}\times\left(1+\frac{ib_1}{x}\tau-\frac{b_2}{x^2}\tau^2-\frac{ib_3}{x^3}\tau^3+\cdots\right)d\tau. \tag{7}$$

The choice of a contour of integration along the path of steepest descent through the saddle point allows us to choose ∞ as the upper limit. Since

$$\int_0^{\infty}e^{-\tau}\tau^{\nu}d\tau=\Gamma(\nu+1)$$

we obtain

$$I_0\sim\frac{\exp\left[ix(1-p)^{\frac{1}{2}}+i\pi/4\right]}{\pi x(xp)^{\frac{1}{2}}(1-p)^{\frac{1}{4}}}\left[\Gamma(1/2)+\frac{ib_1}{x}\Gamma(3/2)-\frac{b_2}{x^2}\Gamma(5/2)-\frac{ib_3}{x^3}\Gamma(7/2)+\cdots\right], \tag{8}$$

by choosing $(-i)^{\frac{1}{2}}=e^{-i\pi/4}$.

A similar term for the contribution from the neighborhood of $\beta=\pi$ can be obtained in the same way. By defining a new variable

$$t_1=f(\beta)-f(\pi)=(1-p\cos\beta)^{\frac{1}{2}}-(1+p)^{\frac{1}{2}}, \tag{9}$$

it is then found that

$$\sin\beta(t_1)=\frac{2(1+p)^{\frac{1}{4}}}{p^{\frac{1}{2}}}it_1^{\frac{1}{2}}\left(1+\frac{(2+3p)t_1}{2p(1+p)^{\frac{1}{2}}}+\frac{t_1^2}{p}+\frac{t_1^3}{4p(1+p)^{\frac{1}{2}}}\right)^{\frac{1}{2}}, \tag{10}$$

$$=\frac{2(1+p)^{\frac{1}{4}}}{p^{\frac{1}{2}}}it_1^{\frac{1}{2}}\Big/\sum_{n=0}^{\infty}b_n't_1^n.$$

We finally obtain

$$I_\tau\sim\frac{\exp\left[ix(1+p)^{\frac{1}{2}}-i\pi/4\right]}{\pi x(px)^{\frac{1}{2}}(1+p)^{\frac{1}{4}}}\times\left[\Gamma(1/2)+\frac{ib_1'}{x}\Gamma(3/2)-\frac{b_2'}{x^2}\Gamma(5/2)-\frac{ib_3'}{x^3}\Gamma(7/2)+\cdots\right]. \tag{11}$$

[2] P. Debye, Math. Ann. **67**, 535 (1909).

We now have the complete evaluation of the original integral (3) in terms of the contributions from the two saddle points. It is the imaginary part of

$$\frac{\exp\left[ix(1-p)^{\frac{1}{2}}+i\pi/4\right]}{x^{\frac{1}{2}}(p\pi)^{\frac{1}{2}}(1-p)^{\frac{1}{4}}}\times\left(1+\frac{ib_1}{2x}-\frac{3b_2}{4x^2}-\frac{15ib_3}{8x^3}+\cdots\right)+\frac{\exp\left[ix(1+p)^{\frac{1}{2}}-i\pi/4\right]}{x^{\frac{1}{2}}(p\pi)^{\frac{1}{2}}(1+p)^{\frac{1}{4}}}\times\left(1+\frac{ib_1'}{2x}-\frac{3b_2'}{4x^2}-\frac{15ib_3'}{8x^3}+\cdots\right), \quad (12)$$

and taking the imaginary part we have,

$$I\sim\frac{1}{(\pi p)^{\frac{1}{2}}x^{\frac{1}{2}}}\times[S(x,p,\pi/4)\sigma_1(p)+C(x,p,\pi/4)\sigma_2(p)+S(x,-p,-\pi/4)\sigma_1(-p)+C(x,-p,-\pi/4)\sigma_2(-p)], \quad (13)$$

where

$$S(x,p,\pi/4)=\frac{\sin\left[x(1-p)^{\frac{1}{2}}+\pi/4\right]}{(1-p)^{\frac{1}{4}}},$$

$$C(x,p,\pi/4)=\frac{\cos\left[x(1-p)^{\frac{1}{2}}+\pi/4\right]}{(1-p)^{\frac{1}{4}}},$$

$$\sigma_1(p)=1-\frac{3b_2}{4x^2}+\cdots,$$

$$\sigma_2(p)=\frac{b_1}{2x}-\frac{15b_3}{8x^3}+\cdots,$$

and

$$b_1=\frac{2-3p}{4p(1-p)^{\frac{1}{2}}},\quad b_2=\frac{12-20p+11p^2}{32p^2(1-p)},$$

and

$$b_3=\frac{40-132p+166p^2-79p^3}{128p^3(1-p)^{\frac{1}{2}}}.$$

The Debye formula is obtained if one expresses x and p in terms of s, l_2 and l_1, sets $\sigma_1=1$ and $\sigma_2=0$ in (13), and if the molecule considered has the dimensions such that $l_2^2-l_1^2=4a^2$, where a is the radius of rotation. (An example is the case of a molecule with an identical group rotating at each end of a bond.)

DISCUSSION

It can be shown that the series in (13) are asymptotic in the sense of Poincare.[3] Thus these series are divergent and this property is manifested by an increase in magnitude of successive terms after a finite number of terms of steadily decreasing magnitude have been passed. In applying the series, the terms which are successively increasing are not included and the approximation will be improved by taking more and more of the successively decreasing terms. The magnitude of the error resulting from cutting the series off at a particular term is roughly of the order of magnitude of the next term in the series.

It is customary in using the visual method[4] for studying electron diffraction patterns of gas molecules to calculate theoretical intensity curves from $s=2$ to $s=20$ or further and to attach quantitative significance at s values greater than 5. It is therefore desirable to evaluate the magnitude of successive terms in the asymptotic series in the vicinity of $s=5$ for some typical molecules. (It should be noted however that with improvement in methods for obtaining accurate diffraction intensities, it may be desirable to consider quantitatively the intensities at values of s less than 5.)

In discussing the applicability of the derived series it is somewhat less cumbersome to refer to the complex expression (12). However, the remarks to be made are readily applied to the final form (13). Two different molecules were chosen for discussion. Hexamethylethane was chosen because a study had been made on this molecule by S. H. Bauer and J. Y. Beach[5] using Debye's formula and it represents a very favorable case. The second example concerns the rotation of the 3 and 3′ carbon atoms in biphenyl, and, as will be seen, is less favorable for the application of the Debye formula. In Table I, the magnitude of the second and third terms included under the parentheses of each of the two series in (12) is recorded for three different values of s. The calculations were based on a hexamethylethane

[3] E. T. Whittaker and G. N. Watson, *Modern Analysis* (The Macmillan Company, New York, 1943), American edition, p. 151.

[4] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).

[5] S. H. Bauer and J. Y. Beach, J. Am. Chem. Soc. **64**, 1142 (1942).

model in which the carbon to carbon distances were taken to be 1.54A and all the angles were considered tetrahedral. In Table II are recorded the same mathematical quantities for the 3 and 3′ carbon atoms in a model of biphenyl which has

TABLE I. Evaluation of successive coefficients in the asymptotic series for a model of hexamethylethane.

	$\left\lvert\frac{b_1}{2x}\right\rvert$	$\left\lvert\frac{3b_2}{4x^2}\right\rvert$	$\left\lvert\frac{b_1'}{2x}\right\rvert$	$\left\lvert\frac{3b_2'}{4x^2}\right\rvert$
$s=2$	0.05	0.03	0.13	0.06
$s=5$	0.02	0.005	0.05	0.01
$s=10$	0.01	0.001	0.03	0.002

regular benzene rings with a carbon to carbon distance in the ring taken as 1.39A and a separation between the rings of 1.52A.

Whereas these two examples are by no means exhaustive, significant information may be obtained by examining the tables. The values for the terms included in the tables must be compared with unity, the leading term in the series, and thus the approximate magnitude of the error in omitting successive terms is readily obtained. For instance, for hexamethylethane the second term of the first series in expression (12) is only about 2 percent of the first term for $s=5$. The second term in the second series for $s=2$ is about 13 percent of the first but this is in a region which is insignificant so far as the visual method is concerned. However for biphenyl in Table II, we see that the third term is larger than the second for $s=2$ and so calculations would include only the second term introducing a rather large error. It is also seen that rather large errors occur in omitting successive terms in the region of $s=5$ to 10.

CONCLUSIONS

Several conclusions can be drawn:

1. Consistent with the spirit of the saddle point method, the accuracy of the asymptotic evaluation increases as s increases.

2. The asymptotic series may be used to estimate the error involved in using the Debye formula and affords a scheme for reducing the error by utilizing additional terms.

3. When the rotating atoms are far apart, the leading terms in the series may decrease in magnitude more slowly. This is illustrated in the case of biphenyl where the effect of the smaller value of p as compared to the value in hexamethylethane more than compensates for the effect of the increase in the value of x due to the larger separation. Since the barriers which restrict rotation are smaller when the rotating groups are farther apart, we can expect that the asymptotic series will find its greatest application in such cases.

TABLE II. Evaluation of successive coefficients in the asymptotic series for a model of biphenyl (re: 3,3′ carbon atoms).

	$\left\lvert\frac{b_1}{2x}\right\rvert$	$\left\lvert\frac{3b_2}{4x^2}\right\rvert$	$\left\lvert\frac{b_1'}{2x}\right\rvert$	$\left\lvert\frac{3b_2'}{4x^2}\right\rvert$
$s=2$	0.23	0.28	0.28	0.32
$s=5$	0.09	0.05	0.11	0.05
$s=10$	0.05	0.01	0.06	0.01

ACKNOWLEDGMENT

I wish to express my appreciation to Professor Otto Laporte for his help in deriving the asymptotic series.